Supporting Information

Surrogates of 2,2'-Bipyridine Designed to Chelate Ag(I) and Create Metallotectons for Engineering Hydrogen-Bonded Crystals

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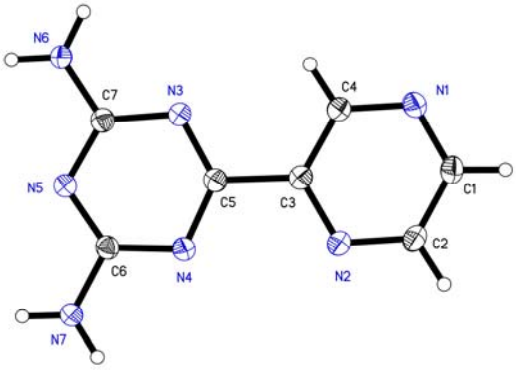

Figure S1. Thermal atomic displacement ellipsoid plot of the structure of crystals of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) grown from DMSO/MeCN. Ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

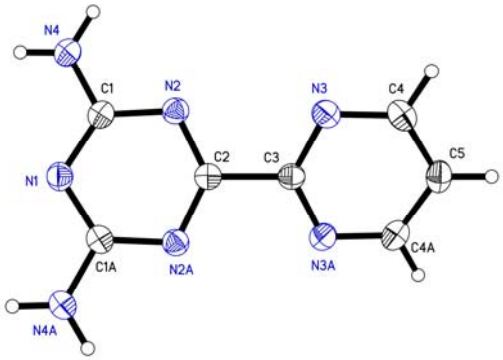

Figure S2. Thermal atomic displacement ellipsoid plot of the structure of crystals of 6-(pyrimidin-2-yl)-1,3,5-triazine-2,4-diamine (**3**) grown from DMSO/CH_2Cl_2. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

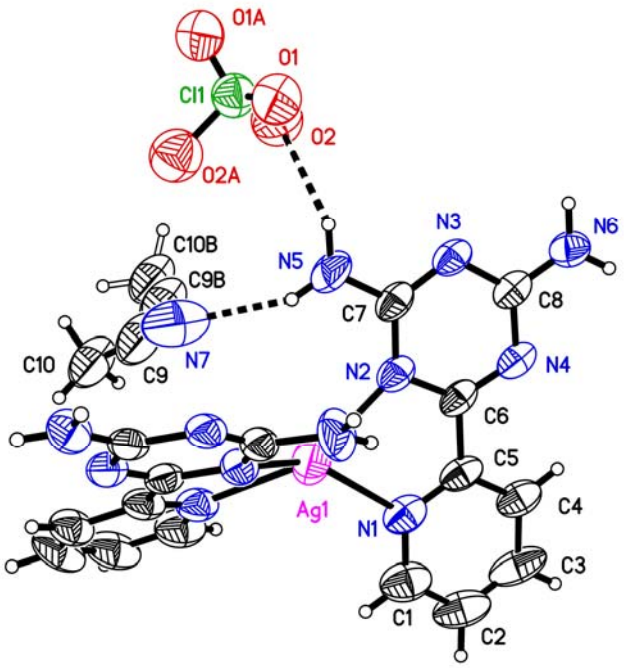

Figure S3. Thermal atomic displacement ellipsoid plot of the structure of crystals of the solvated form of the 2:1 complex of 6-(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (**1**) with $AgClO_4$ grown from DMSO/MeCN. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, hydrogen atoms are represented by a sphere of arbitrary size, and hydrogen bonds are represented by broken lines.

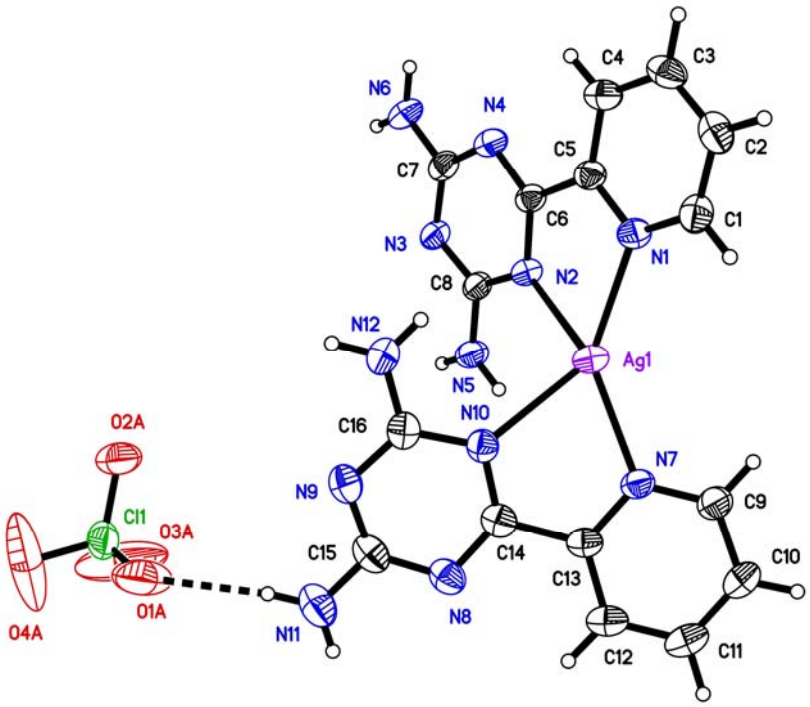

Figure S4. Thermal atomic displacement ellipsoid plot of the structure of crystals of the unsolvated form of the 2:1 complex of 6-(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (**1**) with $AgClO_4$ grown from DMSO/MeCN. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, hydrogen atoms are represented by a sphere of arbitrary size, and hydrogen bonds are represented by broken lines.

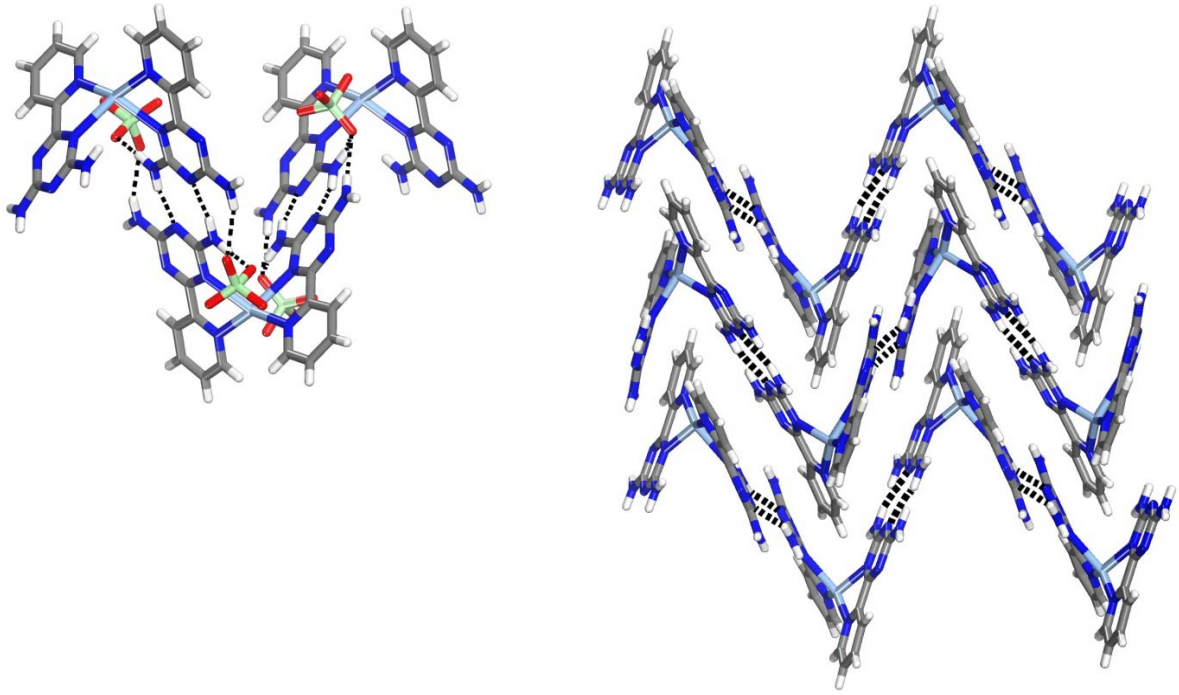

Figure S5. Supplementary views of the structure of crystals of the unsolvated form of 2:1 complex of 6-(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (**1**) with $AgClO_4$ grown from DMSO/MeCN. (a) Alternating chains of cationic complex **9** and its enantiomer, which are held together by hydrogen bonding of DAT groups according to motif **I**, reinforced by hydrogen bonding involving bridging perchlorate. (b) Stacking of corrugated sheets. In both views, hydrogen bonds are represented by broken lines. Carbon atoms are shown in gray, hydrogen atoms in white, chlorine atoms in pale green, nitrogen atoms in dark blue, oxygen atoms in red, and silver atoms in medium blue.

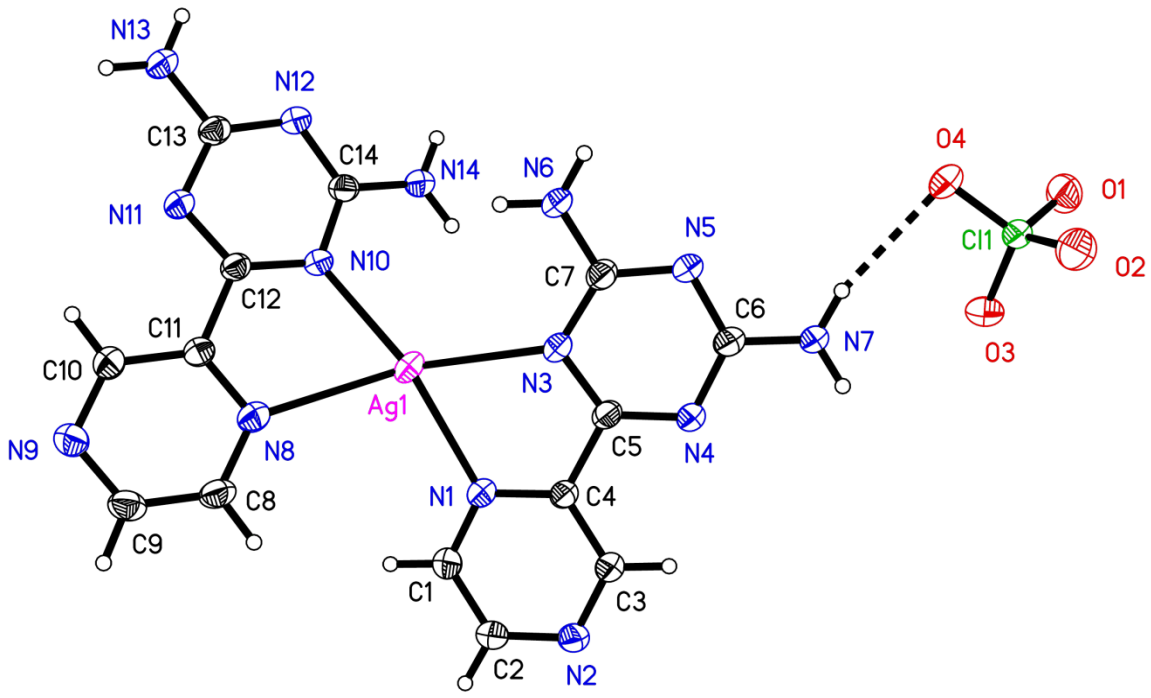

Figure S6. Thermal atomic displacement ellipsoid plot of the structure of crystals of the 2:1 complex of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) with $AgClO_4$ grown from DMSO/MeCN. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, hydrogen atoms are represented by a sphere of arbitrary size, and hydrogen bonds are represented by broken lines.

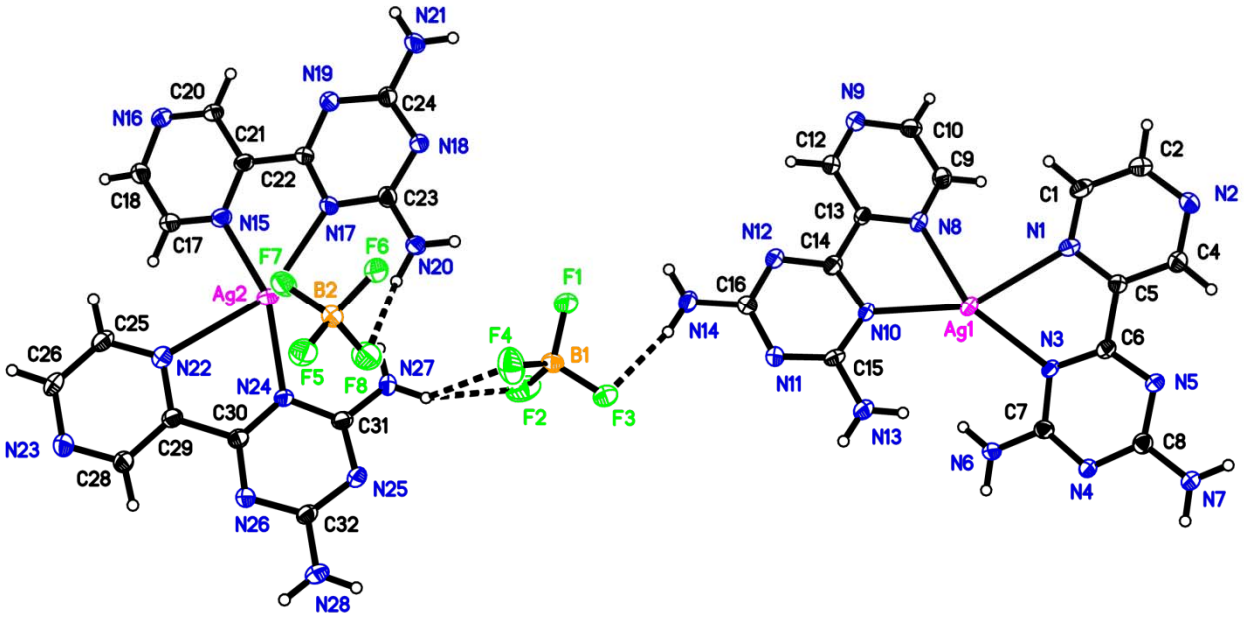

Figure S7. Thermal atomic displacement ellipsoid plot of the structure of crystals of the 2:1 complex of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) with $AgBF_4$ grown from DMSO/MeCN. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, hydrogen atoms are represented by a sphere of arbitrary size, and hydrogen bonds are represented by broken lines.

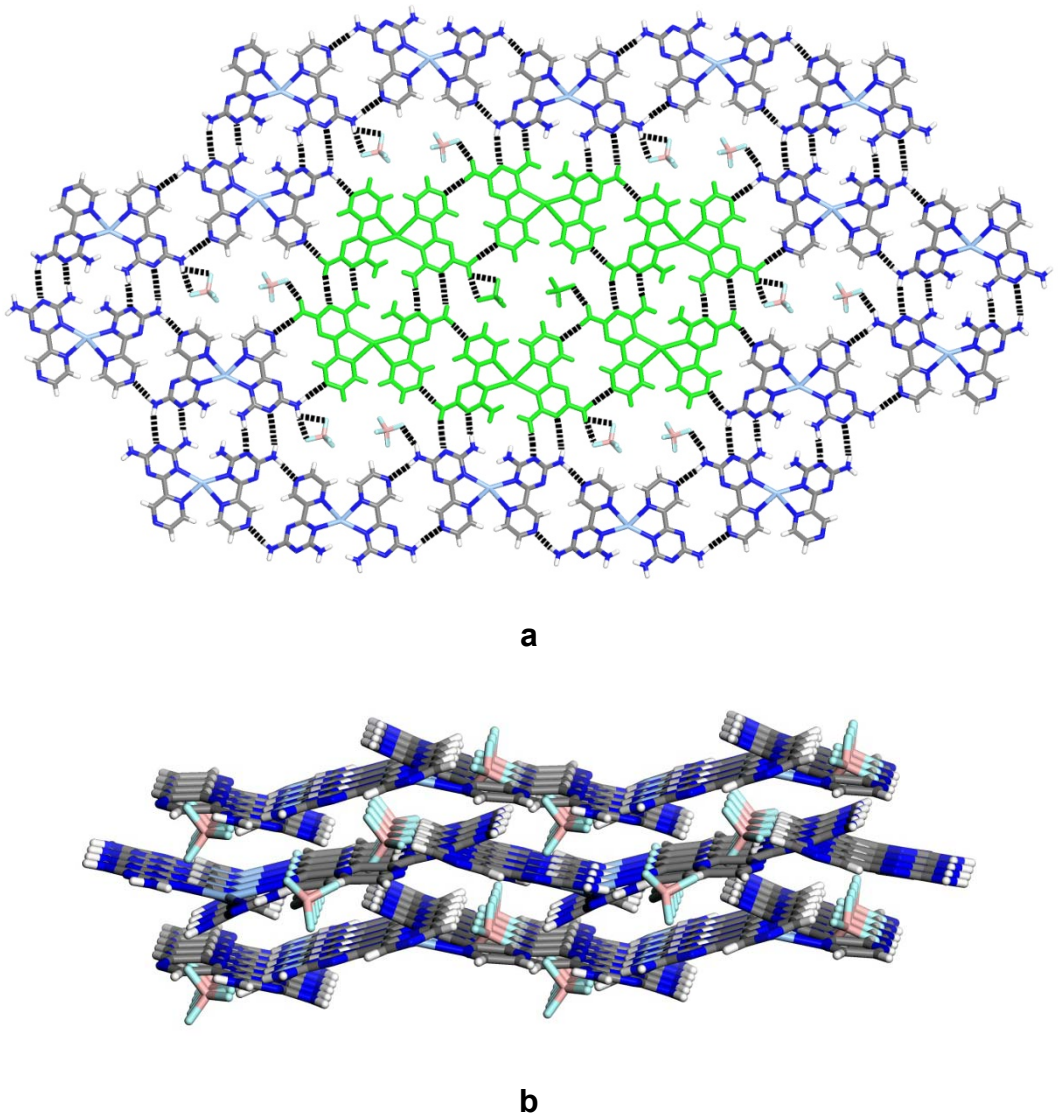

Figure S8. Supplementary views of the structure of crystals of the 2:1 complex of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) with $AgBF_4$ grown from DMSO/MeCN. (a) View of a hydrogen-bonded sheet, with a hexameric rosette highlighted in green. (b) View showing the stacking of three adjacent sheets. Unless noted otherwise, carbon atoms are shown in gray, hydrogen atoms in white, boron atoms in rose, fluorine atoms in light blue, nitrogen atoms in dark blue, and silver atoms in medium blue.

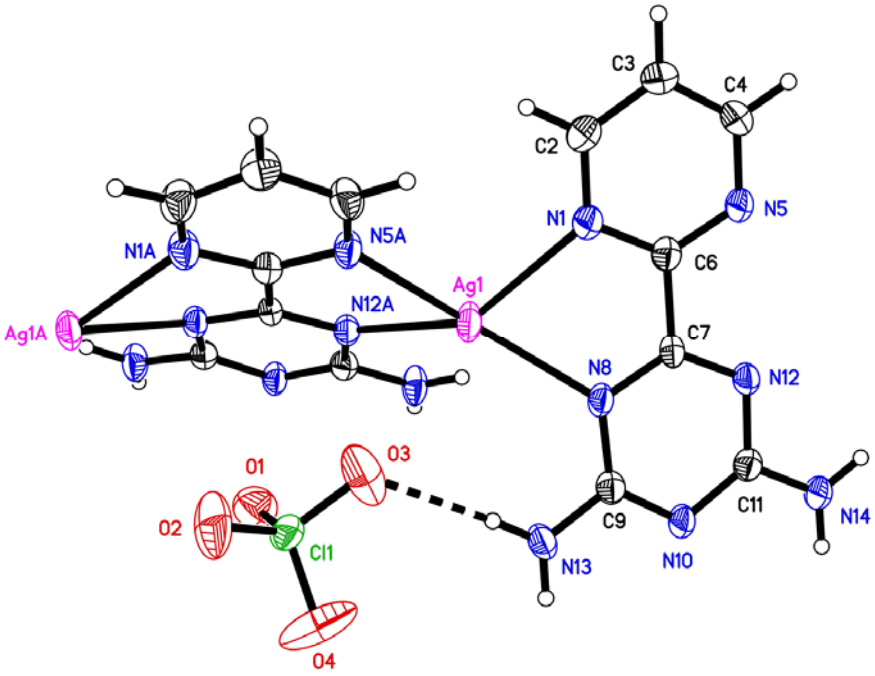

Figure S9. Thermal atomic displacement ellipsoid plot of the structure of crystals of the 1:1 complex of 6-(pyrimidin-2-yl)-1,3,5-triazine-2,4-diamine (**3**) with $AgClO_4$ grown from DMSO/MeOH. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, hydrogen atoms are represented by a sphere of arbitrary size, and hydrogen bonds are represented by broken lines.

Homogeneity of Bulk Crystalline Samples

In all structural studies, experimental powder X-ray diffraction patterns were recorded for each bulk crystalline sample and then compared with those calculated from single-crystal X-ray diffraction data. In the case of the solvated form of the 2:1 complex of 6-(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (**1**) with $AgClO_4$, the crystals proved to be unstable, and the experimental and calculated powder diffraction patterns were different. In all other cases, the patterns were similar, and detailed comparisons confirmed that the single-crystal specimens selected for structural analysis were representative of the bulk crystalline samples from which they were chosen. Experimental powder X-ray diffraction patterns were recorded using one of the following two instruments:

1) Bruker D8 Discover diffractometer with GADDS HTS, using graphite monochromatized Cu Kα radiation generated at 40 kV and 40 mA, working in reflection mode. The 2D general area detector was positioned at a distance of 15 cm from the powder sample, which was placed on a glass plate. This allowed simultaneous collection of data over an angular domain up to 35° in 2θ. Measurements were carried out at 293 K in coupled scan mode (θ-θ geometry). Four separate images (diffraction arcs) were collected (scanning time: 5 min/image), and intensity along each arc was integrated to create the 1D powder pattern of intensity versus 2θ, over the angular range $10° < 2\theta < 105°$.

2) Single-crystal Bruker Microstar diffractometer mounted with an FR591 rotating anode generator, Helios optics and a 2D Pt135 CCD detector, working in transmission mode. A small amount of ground sample was mounted in a fiber loop, and the diffraction patterns were recorded at 150 K by phi-scan over five different detector positions, merged, and integrated to give the 1D powder diffraction pattern.

Structural data from single-crystal analyses were used to calculate theoretical powder X-ray diffraction patterns with the aid of Mercury software.[1] Peak fitting and the refinement of lattice parameters were carried out using TOPAS software,[2] and Pawley fitting was applied to the powder X-ray diffraction patterns. The quality of the refinement was checked by evaluating the weighted agreement factor R_{wp}, which was calculated using background-subtracted intensity data as

$$R_{wp} = \sqrt{\frac{\sum w(Yo - Yc)^2}{\sum w(Yo - Bkg)^2}}$$

where *Y*o is the observed intensity, *Y*c is the calculated intensity, *Bkg* is the background intensity, and *w* is the weighting factor defined by $w = 1/\sigma(Yo)^2$, $\sigma(Yo)$ being the error in the measured intensity.[2]

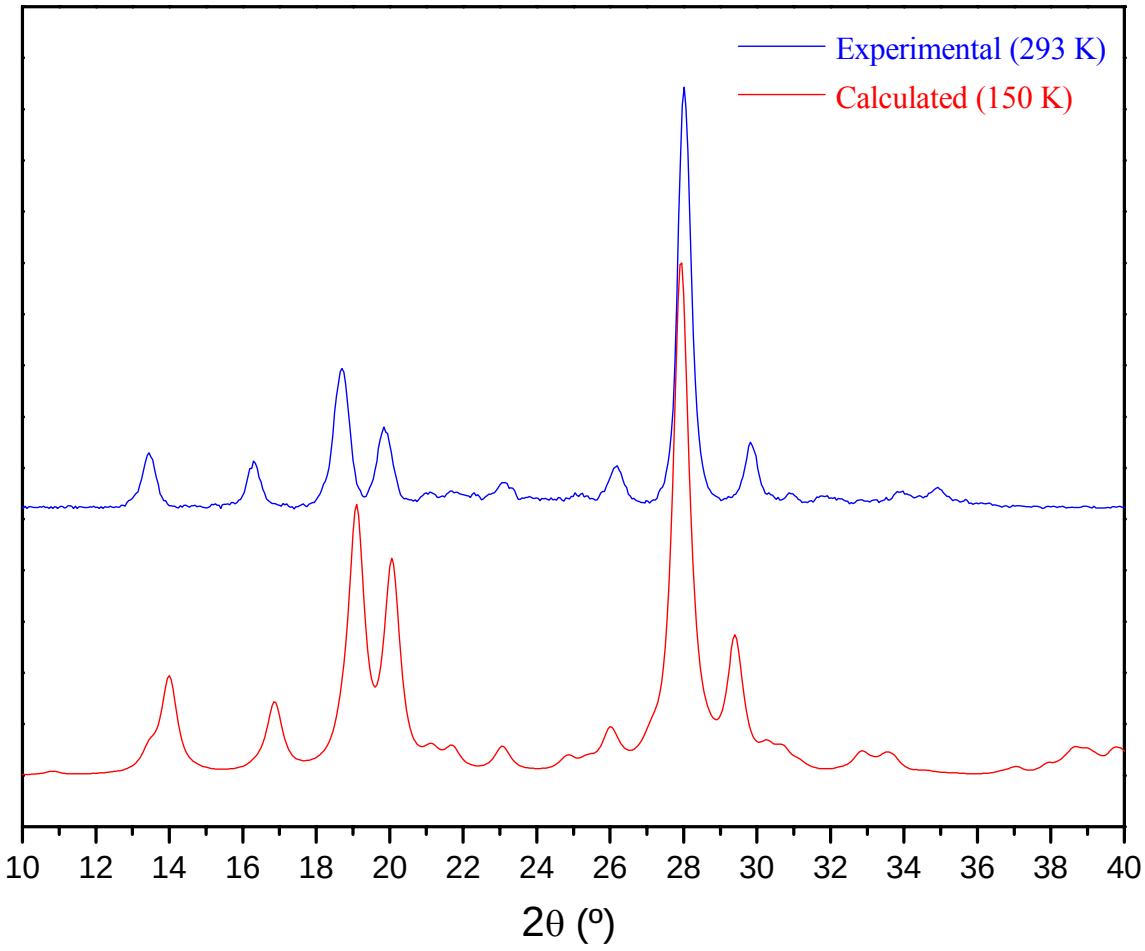

Figure S10. Comparison between experimental (collected using D8 Discover) and calculated powder X-ray diffraction patterns for crystals of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) grown from DMSO/MeCN. The *x* axis of the experimental pattern was shifted to minimize the slight angular shift due to the effect of temperature. The two diffractograms are closely similar, confirming that the bulk crystalline sample consists of a single phase.

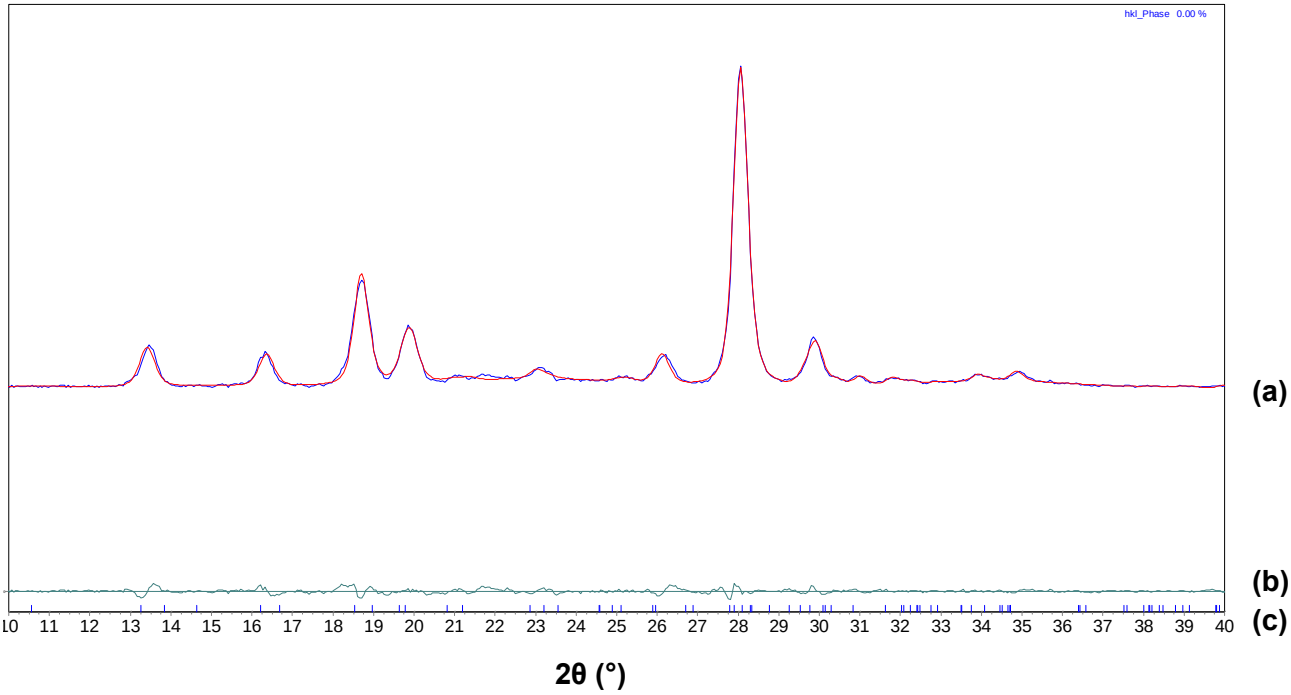

Figure S11. (a) Simulated powder X-ray diffraction pattern of crystals of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) grown from DMSO/MeCN (red curve), as determined by Pawley fitting of the experimental powder X-ray diffraction pattern (nearly superimposed blue curve). (b) Difference between experimental and calculated intensities. (c) Position of calculated reflections.

Table S1. Crystallographic Data for Crystals of 6-(Pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) Grown from DMSO/MeCN, as Determined by Pawley Fitting of Powder X-Ray Diffraction Data at 293 K.

compound	**2**
composition	$C_7H_7N_7$
temperature (K)	293
crystal system	monoclinic
space group	$P2_1/n$
a (Å)	9.303(11)
b (Å)	6.859(55)
c (Å)	13.159(88)
α (º)	90
β (º)	103.73(72)
γ (º)	90
V (Å^3)	815.8(13)
Z	4
R_{wp}	5.35

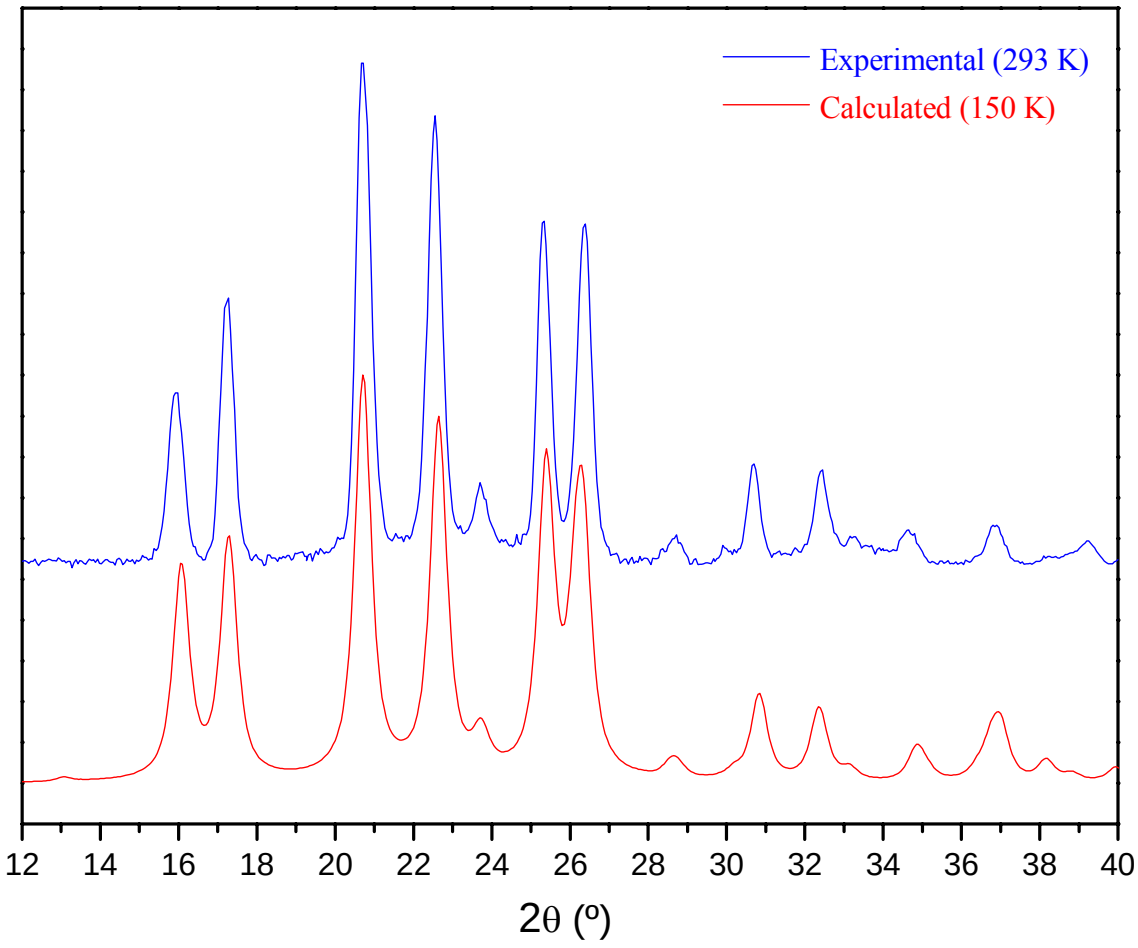

Figure S12. Comparison between experimental (collected using D8 Discover) and calculated powder X-ray diffraction patterns for crystals of 6-(pyrimidin-2-yl)-1,3,5-triazine-2,4-diamine (**3**) grown from DMSO/CH_2Cl_2. The *x* axis of the experimental pattern was shifted to minimize the slight angular shift due to the effect of temperature. The two diffractograms are closely similar, confirming that the bulk crystalline sample consists of a single phase.

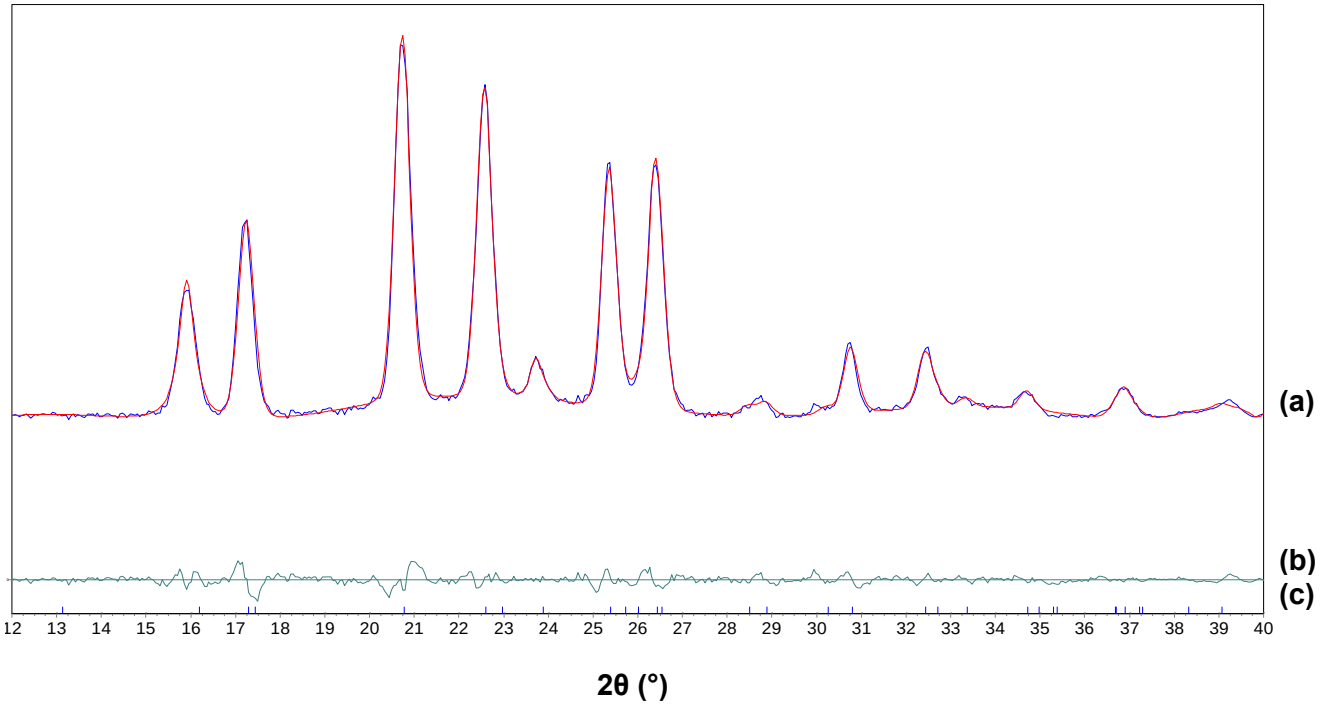

Figure S13. (a) Simulated powder X-ray diffraction pattern of crystals of 6-(pyrimidin-2-yl)-1,3,5-triazine-2,4-diamine (**3**) grown from DMSO/CH_2Cl_2 (red curve), as determined by Pawley fitting of the experimental powder X-ray diffraction pattern (nearly superimposed blue curve). (b) Difference between experimental and calculated intensities. (c) Position of calculated reflections.

Table S2. Crystallographic Data for Crystals of 6-(Pyrimidin-2-yl)-1,3,5-triazine-2,4-diamine (**3**) Grown from DMSO/CH_2Cl_2**,** as Determined by Pawley Fitting of Powder X-Ray Diffraction Data at 293 K.

compound	**3**
composition	$C_7H_7N_7$
temperature (K)	293
crystal system	tetragonal
space group	$P4_32_12$
a (Å)	7.738(51)
b (Å)	7.738(51)
c (Å)	13.689(66)
α (º)	90
β (º)	90
γ (º)	90
V (Å^3)	819.8(11)
Z	4
R_{wp}	3.78

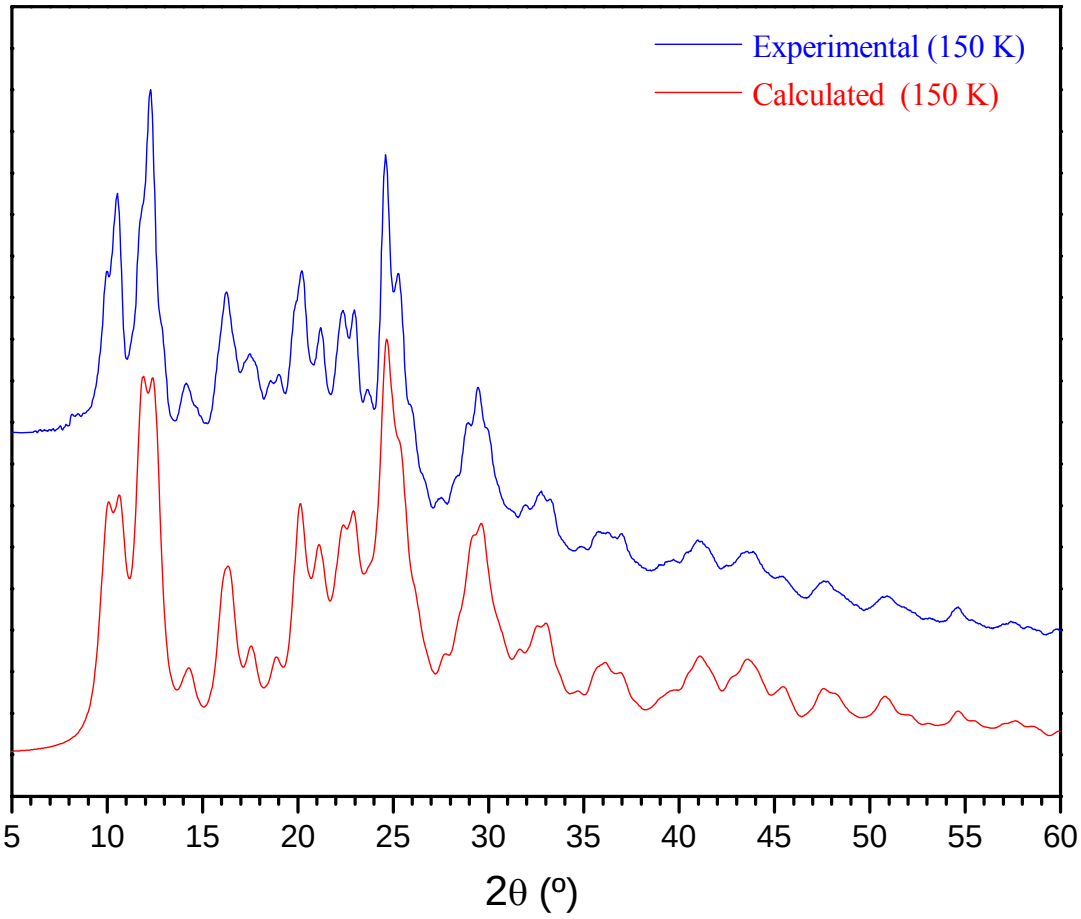

Figure S14. Comparison between experimental (collected using a Bruker Microstar diffractometer) and calculated powder X-ray diffraction patterns for crystals of the unsolvated form of the 2:1 complex of 6-(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (**1**) with $AgClO_4$ grown from DMSO/MeCN. The two diffractograms are closely similar, confirming that the bulk crystalline sample consists of a single phase.

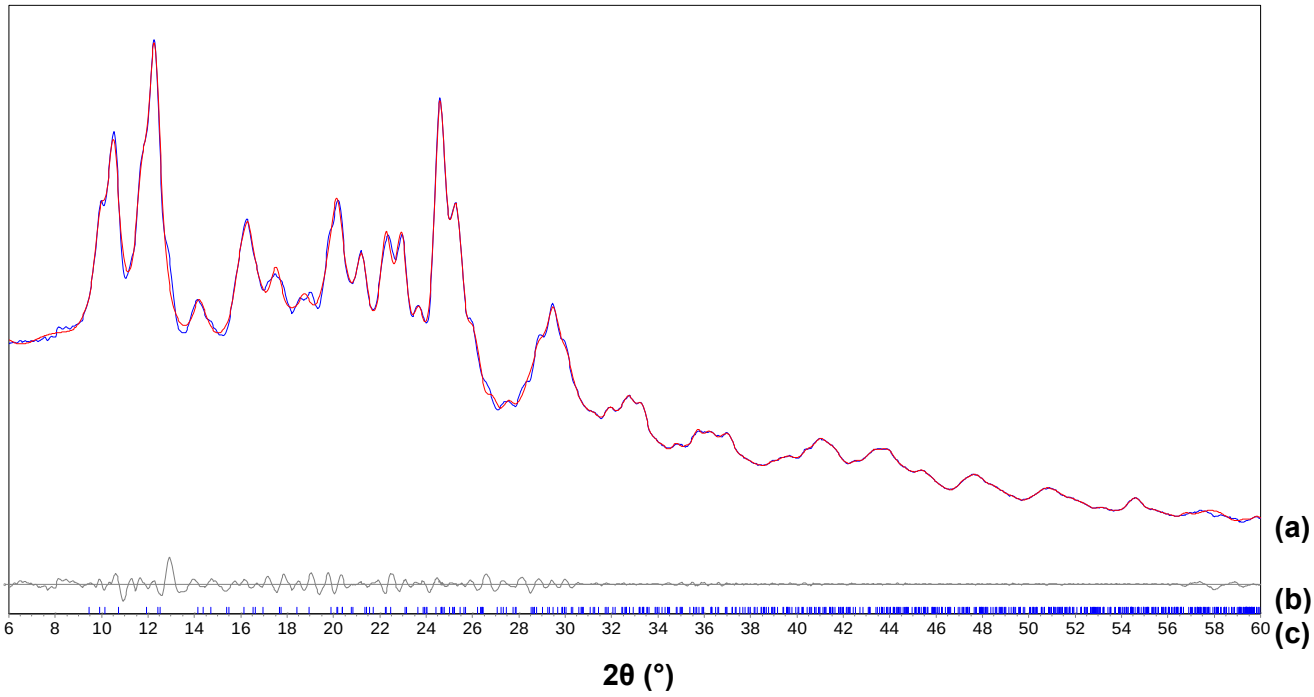

Figure S15. (a) Simulated powder X-ray diffraction pattern of crystals of the unsolvated form of the 2:1 complex of 6-(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (**1**) with $AgClO_4$ grown from DMSO/MeCN (red curve), as determined by Pawley fitting of the experimental powder X-ray diffraction pattern (nearly superimposed blue curve). (b) Difference between experimental and calculated intensities. (c) Position of calculated reflections.

Table S3. Crystallographic Data for Crystals of the Unsolvated Form of the 2:1 Complex of 6-(Pyridin-2-yl)-1,3,5-triazine-2,4-diamine (**1**) with $AgClO_4$ Grown from DMSO/MeCN, as Determined by Pawley Fitting of Powder X-Ray Diffraction Data at 150 K.

compound	$[Ag(\mathbf{1})_2](ClO_4)$
composition	$C_{16}H_{16}AgClN_{12}O_4$
temperature (K)	150
crystal system	monoclinic
space group	$P2_1/n$
a (Å)	11.516(59)
b (Å)	14.125(42)
c (Å)	12.517(43)
α (º)	90
β (º)	93.171(59)
γ (º)	90
V (Å^3)	2033(14)
Z	4
R_{wp}	2.26

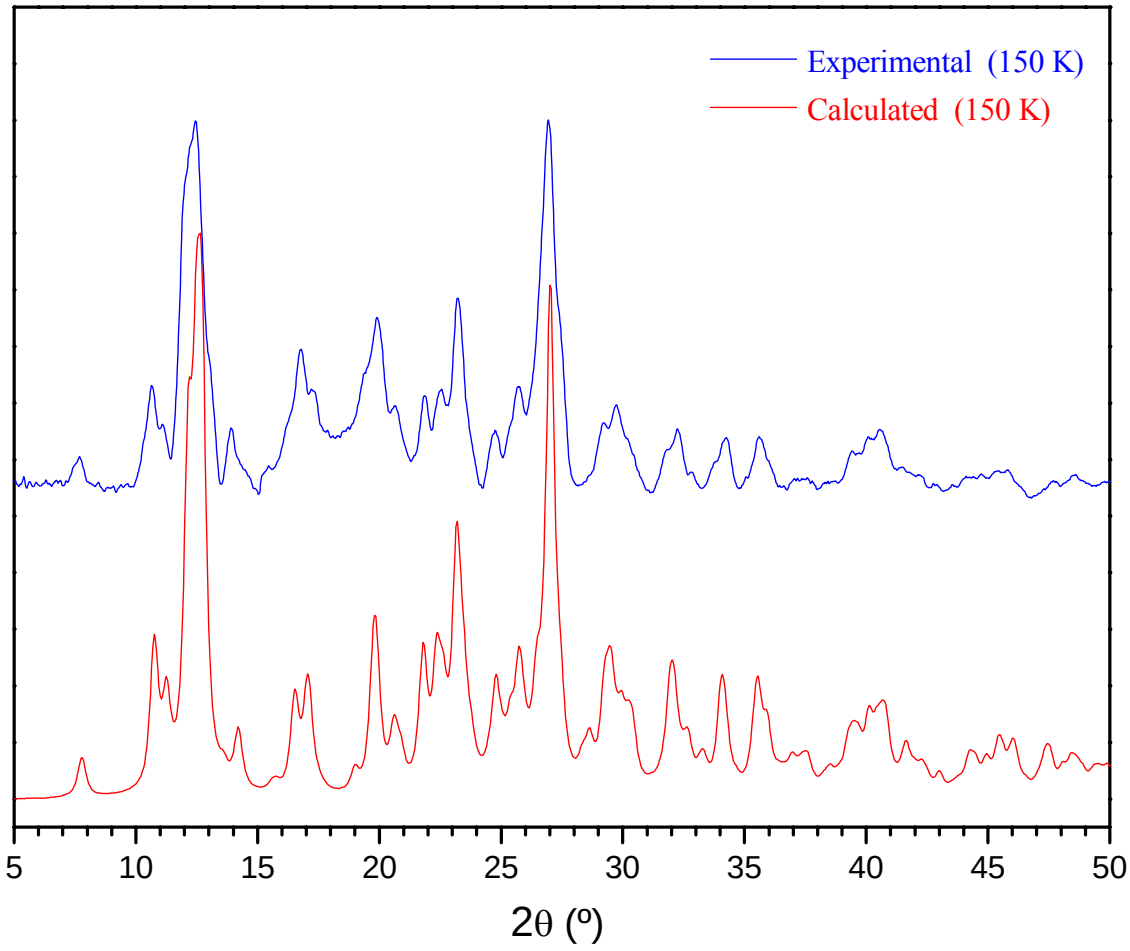

Figure S16. Comparison between experimental (collected using a Bruker Microstar diffractometer) and calculated powder X-ray diffraction patterns for crystals of the 2:1 complex of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) with $AgClO_4$ grown from DMSO/MeCN. The two diffractograms are closely similar, confirming that the bulk crystalline sample consists of a single phase.

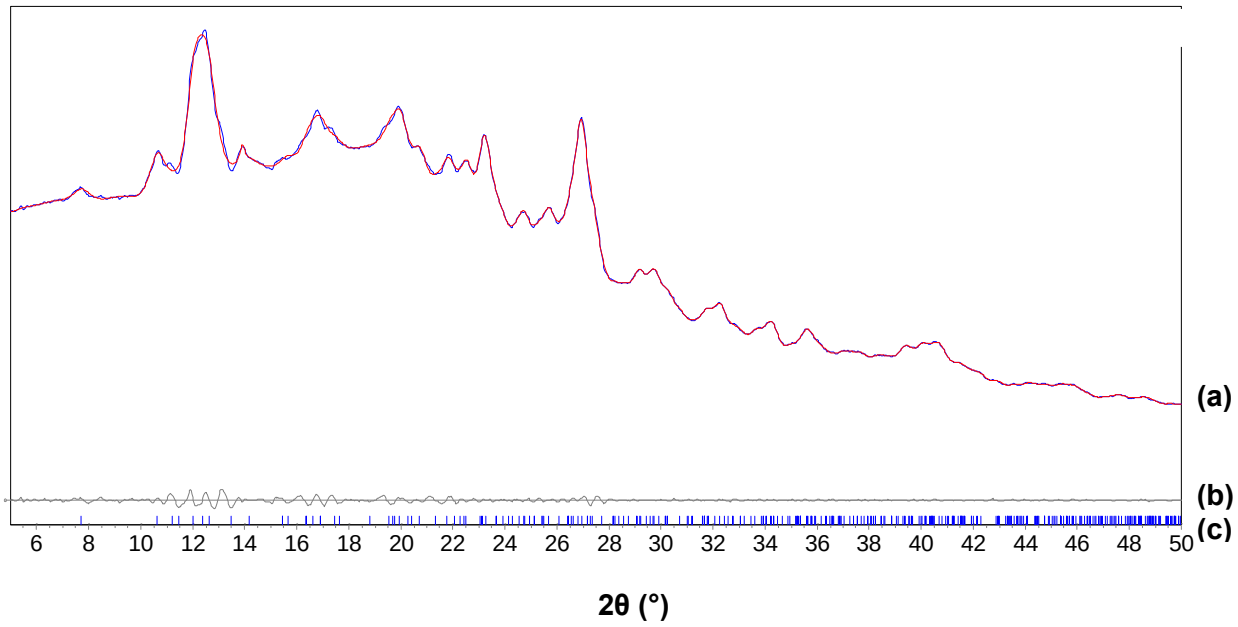

Figure S17. (a) Simulated powder X-ray diffraction pattern of crystals of the 2:1 complex of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) with $AgClO_4$ grown from DMSO/MeCN (red curve), as determined by Pawley fitting of the experimental powder X-ray diffraction pattern (nearly superimposed blue curve). (b) Difference between experimental and calculated intensities. (c) Position of calculated reflections.

Table S4. Crystallographic Data for Crystals of the 2:1 Complex of 6-(Pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) with $AgClO_4$ Grown from DMSO/MeCN, as Determined by Pawley Fitting of Powder X-Ray Diffraction Data at 150 K.

compound	$[Ag(\mathbf{2})_2](ClO_4)$
composition	$C_{14}H_{14}AgClN_{14}O_4$
temperature (K)	150
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	7.743(23)
b (Å)	16.613(64)
c (Å)	15.790(62)
α (º)	90
β (º)	93.85(28)
γ (º)	90
V (Å^3)	2027(13)
Z	4
R_{wp}	2.64

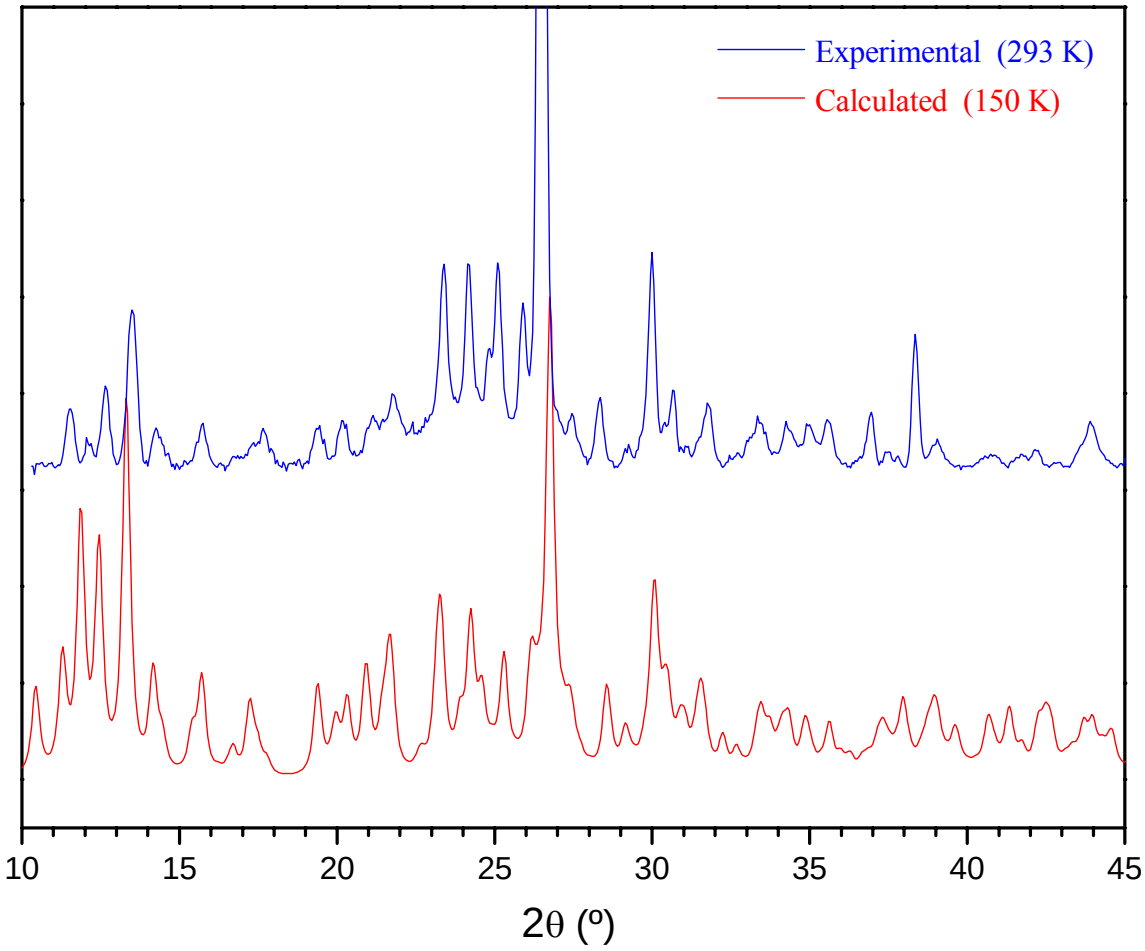

Figure S18. Comparison between experimental (collected using D8 Discover) and calculated powder X-ray diffraction patterns for crystals of the 2:1 complex of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) with $AgBF_4$ grown from DMSO/MeCN. The *x* axis of the experimental pattern was shifted to minimize the slight angular shift due to the effect of temperature. The two diffractograms are closely similar, confirming that the bulk crystalline sample consists of a single phase.

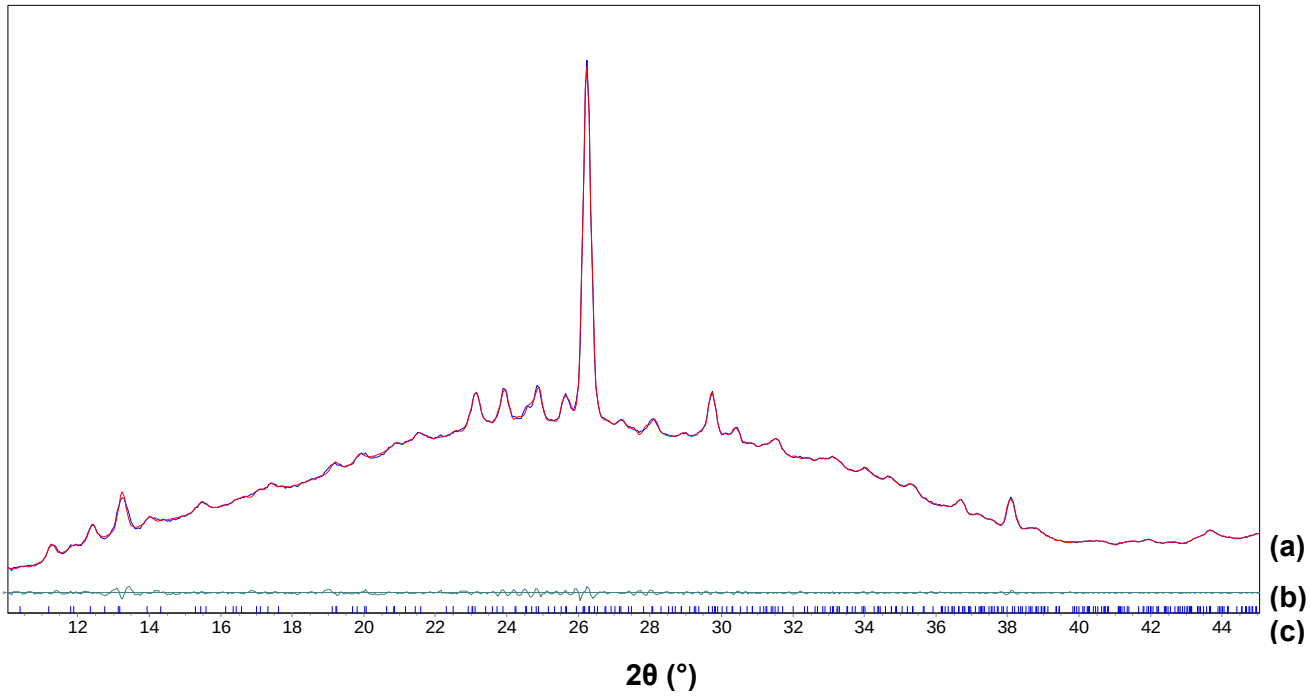

Figure S19. (a) Simulated powder X-ray diffraction pattern of crystals of the 2:1 complex of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) with $AgBF_4$ grown from DMSO/MeCN (red curve), as determined by Pawley fitting of the experimental powder X-ray diffraction pattern (nearly superimposed blue curve). (b) Difference between experimental and calculated intensities. (c) Position of calculated reflections.

Table S5. Crystallographic Data for Crystals of the 2:1 Complex of 6-(Pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (**2**) with $AgBF_4$ Grown from DMSO/MeCN, as determined by Pawley Fitting of Powder X-Ray Diffraction Data at 293 K.

compound	$[Ag(\mathbf{2})_2](BF_4)$
composition	$C_{14}H_{14}AgBF_4N_{14}$
temperature (K)	293
crystal system	monoclinic
space group	$P2_1$
a (Å)	7.4499(40)
b (Å)	15.796(12)
c (Å)	17.048(12)
α (º)	90
β (º)	92.535(84)
γ (º)	90
V (Å^3)	2004.1(24)
Z	4
R_{wp}	4.35

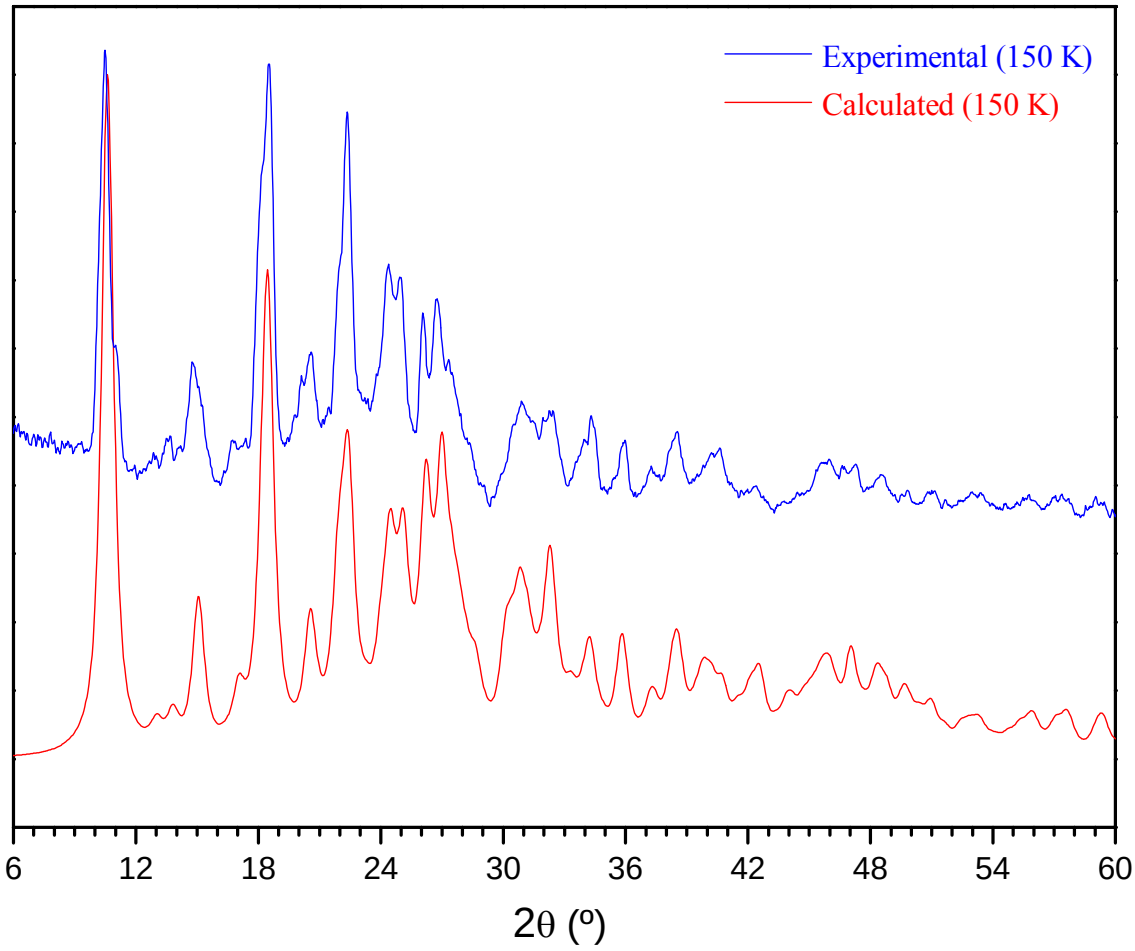

Figure S20. Comparison between experimental (collected using a Bruker Microstar diffractometer) and calculated powder X-ray diffraction patterns for crystals of the 1:1 complex of 6-(pyrimidin-2-yl)-1,3,5-triazine-2,4-diamine (**3**) with $AgClO_4$ grown from DMSO/MeOH. The two diffractograms are closely similar, confirming that the bulk crystalline sample consists of a single phase.

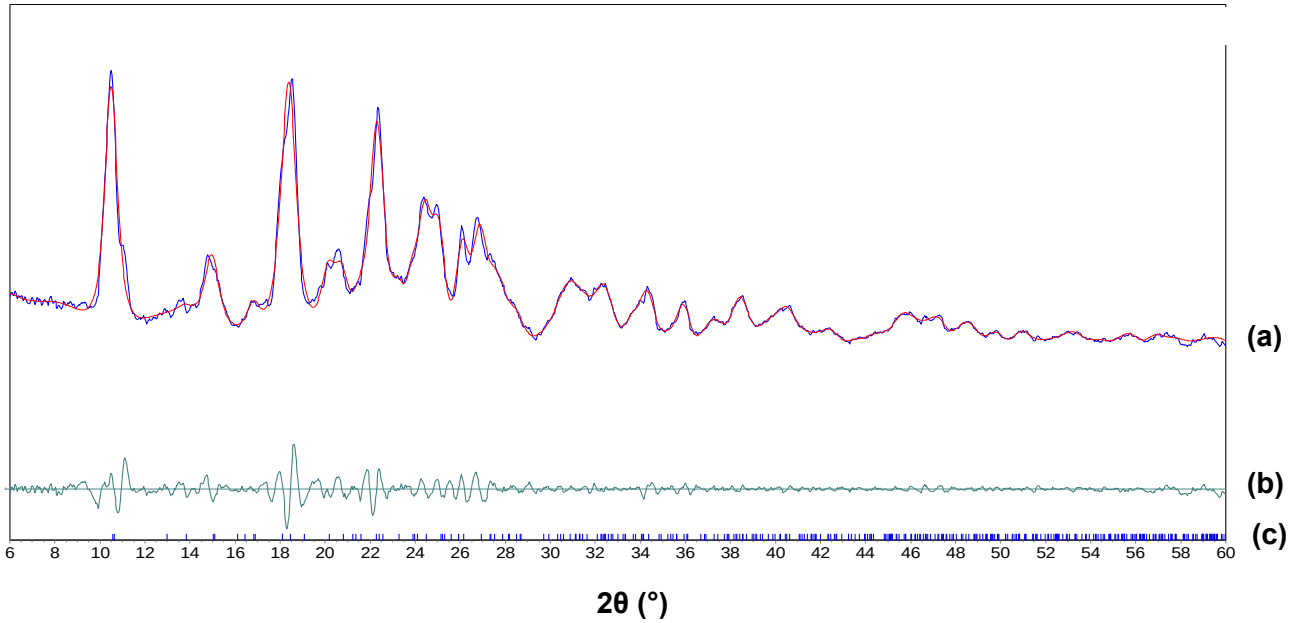

Figure S21. (a) Simulated powder X-ray diffraction pattern of crystals of the 1:1 complex of 6-(pyrimidin-2-yl)-1,3,5-triazine-2,4-diamine (**3**) with $AgClO_4$ grown from DMSO/MeOH (red curve), as determined by Pawley fitting of the experimental powder X-ray diffraction pattern (nearly superimposed blue curve). (b) Difference between experimental and calculated intensities. (c) Position of calculated reflections.

Table S6. Crystallographic Data for Crystals of the 1:1 Complex of 6-(Pyrimidin-2-yl)-1,3,5-triazine-2,4-diamine (**3**) with $AgClO_4$ Grown from DMSO/MeOH, as Determined by Pawley Fitting of Powder X-Ray Diffraction Data at 150 K.

compound	[Ag(**3**)](ClO_4)
composition	$C_7H_7AgClN_7O_4$
temperature (K)	150
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	8.564(62)
b (Å)	11.725(64)
c (Å)	12.054(96)
α (º)	90
β (º)	102.36(27)
γ (º)	90
V (Å^3)	1182(14)
Z	4
R_{wp}	5.89

References

1) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Cryst.* **2006**, *39*, 453-457.
2) Coelho, A. A. *TOPAS User Manual*, Version 3.1 ed.; Bruker-AXS GmbH: Karlsruhe, Germany, 2003.